Synthetic and Structural Studies on Group 13 Complexes containing the $M(CO)_3(\eta\text{-}C_5H_5)$ Fragment (M = Cr or Mo). Part 2.[1] Complexes $[InCl_x\{M(CO)_3(\eta\text{-}C_5H_5)\}_2]^{n-}$ ($x = 1, n = 0$; $x = 2, n = 1$)†

Lucy M. Clarkson,[a] William Clegg,[a] David C. R. Hockless,[a] Nicholas C. Norman,*,[a]
Louis J. Farrugia,[b] Simon G. Bott[c] and Jerry L. Atwood[c]
[a] *Department of Chemistry, The University, Newcastle upon Tyne, NE1 7RU, UK*
[b] *Department of Chemistry, The University, Glasgow, G12 8QQ, UK*
[c] *Department of Chemistry, The University of Alabama, Tuscaloosa, AL 35487, USA*

The synthesis and solution infrared studies of a range of compounds of general formula $[InX(L)\{M(CO)_3(\eta\text{-}C_5H_5)\}_2]$ have been performed where X = Cl or I, L = X, tetrahydrofuran (thf), pyridine (py) and M = Cr, Mo or W. In addition, structures have been determined by X-ray analysis for $[InCl(thf)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$, $[InCl(py)\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]$ and $[NMe_4][InCl_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ and these are discussed and compared with the structures of related complexes.

In the preceding paper[1] we described our results on complexes of the general formula $[E\{M(CO)_3(\eta\text{-}C_5H_5)\}_3]$ (E = In or Tl, M = Cr or Mo). Detailed comparisons were made with previously reported related compounds, but in the Introduction a general overview of complexes containing the heavier Group 13 elements bonded to one or more $M(CO)_3(\eta\text{-}C_5H_5)$ fragments (M = Cr, Mo or W) was also presented and this serves as an appropriate preface to this paper as well. In this report we shall concentrate on our results concerning indium complexes bonded to one or two $M(CO)_3(\eta\text{-}C_5H_5)$ fragments (M = Cr or Mo) which form a continuation of some of our earlier work in this area.[2,3]

Results and Discussion

(*i*) *Synthesis and Solution Studies.*—The compounds which we will be concerned with in this section contain the heterometallic fragments $In(ML_n)_2$ and $In(ML_n)$ where $ML_n = M(CO)_3(\eta\text{-}C_5H_5)$, M = Cr or Mo, and in which the indium centre is also bonded to one or more halogen atoms. The only previous relevant work of which we are aware was carried out by Hsieh and Mays[4] who reported the complexes $[InX\{M(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (X = Cl or Br, M = Mo or W). Three synthetic methods were used, namely the reaction between InX_3 and $2Na[M(CO)_3(\eta\text{-}C_5H_5)]$ in tetrahydrofuran (thf), the insertion of InX into the M–M bond in $[M_2(CO)_6(\eta\text{-}C_5H_5)_2]$ and the reaction between InX and $[Hg\{M(CO)_3(\eta\text{-}C_5H_5)\}_2]$. These authors also reported the complex $[InCl_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}]$ to which we shall return later.

In ref. 2 we reported the reaction between $InCl_3$ and 2 equivalents of $Na[M(CO)_3(\eta\text{-}C_5H_5)]$ (M = Mo or W) which afforded the anionic dichloro complexes $[InCl_2\{M(CO)_3(\eta\text{-}C_5H_5)\}_2]^-$ (M = Mo, **1**; or W, **2**). Compound **1** was characterised by X-ray crystallography as $[Na(thf)_2][InCl_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (hereafter **1a**). These results were compared[2] with those reported by Mays who described the synthesis of $[InCl\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ **3** from a similar reaction. The observed differences were attributed to the different solvent systems used, **1** being recrystallised from thf–hexane whilst **3** was washed with and recrystallised from thf–water (see refs. 2 and 4 for details) which perhaps accounted for the loss of chloride in **3** *vs.* **1**. We have now extended our earlier work to the chromium system and have obtained analogous results. Thus the reaction between $InCl_3$ and 2 equivalents of $Na/K[Cr(CO)_3(\eta\text{-}C_5H_5)]$ afforded, after work-up, pale yellow crystals of the anionic complex $[InCl_2\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]^-$ **4**, an infrared spectrum of which is shown in Fig. 1(*a*) (*cf.* the spectrum of **1a** in ref. 2). Crystals of **4** were found to be isomorphous with **1a** but decayed before a complete X-ray data set could be collected (see Experimental section). Thus although no structural details for **4** are available its formulation as $[Na/K(thf)_2][InCl_2\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]$ *i.e.* **4a**, analogous to **1a**, is proposed on the basis of the unit-cell data.

We shall have more to say about these and other related dichloro anionic complexes later but at this time we will turn to the neutral monochloro species $[InCl\{M(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (M = Mo, **3**; Cr, **5**; or W, **6**). In our hands these complexes were not easily accessible from reactions involving $InCl_3$ and 2 equivalents of the metal carbonylate anion. However, they can all readily be made from the reaction between indium monochloride and the M–M bonded dimers, $[M_2(CO)_6(\eta\text{-}C_5H_5)_2]$. Refluxing a toluene solution of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ with slightly less than 1 equivalent of InCl, which is insoluble in this solvent, afforded a yellow powder after a few hours. This powder was isolated and washed with diethyl ether to remove any excess of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ and then redissolved in thf and crystallised by solvent diffusion using an overlayer of hexane. This procedure afforded clear yellow block-like crystals which were shown to be a thf adduct of **3**, $[InCl(thf)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ **7** by X-ray crystallography (see below). A solution infrared spectrum obtained after dissolving crystals of **7** in thf is shown in Fig. 1(*b*) (infrared numerical and analytical data for this and other new complexes are presented in Table 1, NMR data in Table 2) but an identical spectrum was also obtained from solutions of the crude yellow powder in thf. We suspect that **3**, which precipitates from toluene in the reaction described above, contains chloride bridges between indium centres, possibly as a dimer analogous to the known dimeric structures of $[InCl\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]^5$ and $[InX\{M(CO)_5\}_2]$ (X = Cl, Br or I; M = Mn or Re).[6]

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

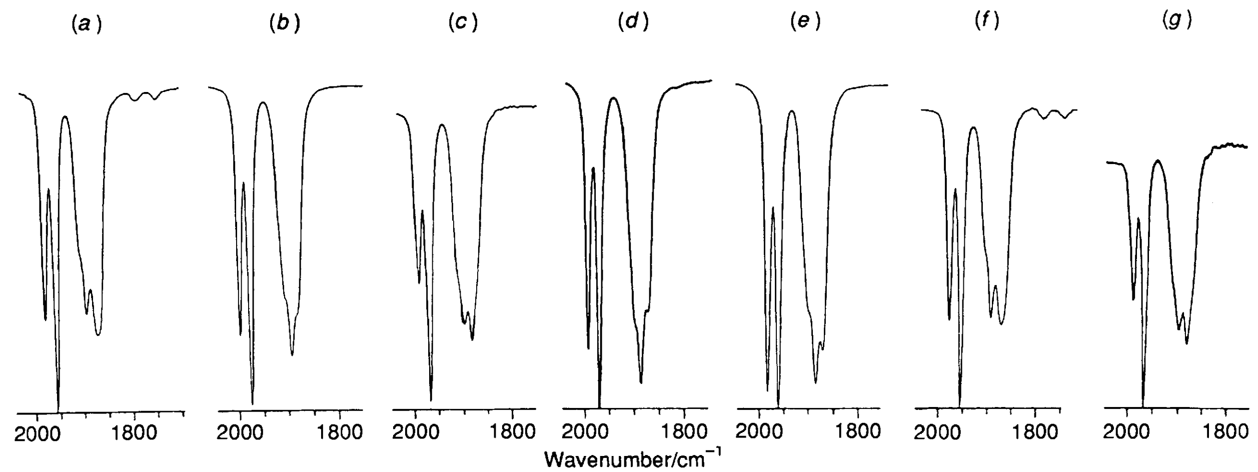
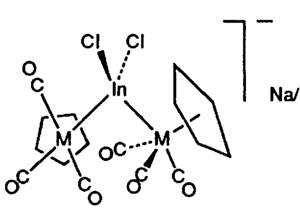
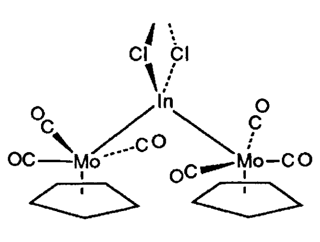


Fig. 1 Solution infrared spectra in the carbonyl stretching region in thf: (*a*) complex **4** in CaF_2, (*b*) **7** in CaF_2, (*c*) **7a** in KBr, (*d*) **8** in CaF_2, (*e*) **9** in CaF_2, (*f*) **9a** in KBr, and (*g*) **10** in CaF_2



M = Cr, **4a**; or Mo, **1a**



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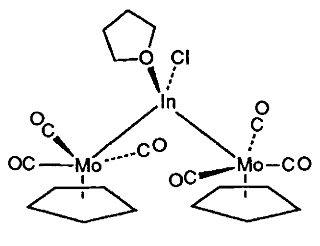

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Dissolution in thf leads to a break-up of the chloride bridges and formation of the thf adduct **7** which can be crystallised from this solvent. Moreover the thf in **7** is sufficiently tightly bound that satisfactory analytical data (Table 1) and ^1H NMR data, with respect to peak integration (Table 2), were obtained even after subjecting solid **7** to vacuum for short periods. In $[InCl\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ we observed similar break-up of chloride bridges on addition of the phosphine PMe_2Ph with concomitant formation of the mononuclear phosphine adduct $[InCl(PMe_2Ph)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$.[5]

All of the above data were fully reproducible except for one feature, that of the solution infrared spectra. On *some* occasions, as we described in a preliminary communication,[3] a different spectrum was observed which is shown in Fig. 1(*c*). This spectrum has been obtained both for the crude product and for crystals obtained from thf–hexane. We shall designate the compound which gives rise to this spectrum as **7a** and numerical infrared data are presented in Table 1, but a striking resemblance in all respects between the Fig. 1(*c*) spectrum and the spectrum we had obtained for **1a** [Table 1 and Fig. 4(*a*) in ref. 2] was obvious. Our initial thoughts therefore, which are briefly described in ref. 3, were that in some reactions between InCl and $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ appreciable quantities of the dichloro anion **1** were formed as opposed to the neutral monochloro species **3**. This was partly correct but the explanation for the above observations had to do with the type of infrared solution cell used. The spectrum of complex **7** obtained in thf in CaF_2 cells is shown in Fig. 1(*b*) whilst that obtained in KBr cells is in Fig. 1(*c*). We suggest, therefore, that in CaF_2, **7** exists, in thf solution, as written but that in a KBr cell a reaction takes place affording a dihalogeno anionic species $[InCl(Br)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]^-$ **7a**, thus accounting for the resemblance of this spectrum, *i.e.* Fig. 1(*c*), to the spectrum seen for **1a**.[2] On one occasion we observed what appeared to be a superposition of both spectra in KBr cells [Fig. 2(*c*) in ref. 3]. This behaviour was similar to what we had observed for the trimolybdenum–indium complex $[In\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$ in thf solution (see ref. 1 and refs. therein), *i.e.* different spectra being observed in KBr and CaF_2 cells.

We next examined the analogous tungsten system and studied the reaction between InCl and $[W_2(CO)_6(\eta\text{-}C_5H_5)_2]$. This reaction requires more forcing conditions and prolonged reflux in toluene was necessary to obtain reasonable yields of complex **6** although yields are always lower than for **3**. Crystallisation of **6** from thf–hexane mixtures afforded clear yellow crystals of what we assume to be $[InCl(thf)\{W(CO)_3(\eta\text{-}C_5H_5)\}_2]$ **8**, but when these crystals were dried they readily lost thf and became opaque. An infrared spectrum of **6** in thf run in CaF_2 cells is shown in Fig. 1(*d*) (data in Table 1) and the resemblance to the spectrum of **7** [Fig. 1(*b*)] is obvious. In thf **6** almost certainly exists as **8** but analytical data (Table 1) on vacuum-dried crystals are consistent with the formula given for **6**.

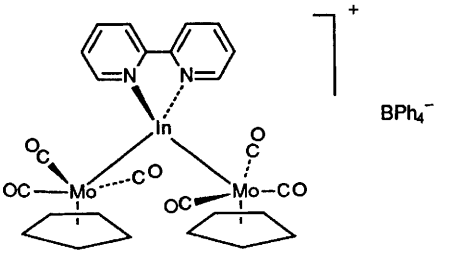
Indium monochloride reacted readily with $[Cr_2(CO)_6(\eta\text{-}C_5H_5)_2]$ in toluene at room temperature to give complex **5** as a yellow powder and clear pale yellow crystals of $[InCl(thf)\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]$ **9** were obtained from thf–hexane. These crystals also readily lost thf when removed from the solvent and dried, and the analytical data (Table 1) are consistent with the formula given for **5**. An infrared spectrum obtained on solutions of some of these crystals in thf in CaF_2 cells is shown in Fig. 1(*e*) (data in Table 1) and the similarity to Fig. 1(*b*) and (*d*) is apparent. Also, in the same way that **6** exists as **8** in thf, **5** is assumed to exist as **9** in this solvent. Again, and as with the molybdenum complexes, solutions of **9** in thf gave a spectrum different from Fig. 1(*e*) when run in KBr cells, **9a**, and this is shown in Fig. 1(*f*). This is identical to the spectrum of **4a** shown in Fig. 1(*a*) and provides support for our view that a halide adduct is formed in KBr.

The reaction between $[In\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$ and 1 equivalent of $HBF_4{\cdot}Et_2O$ in the presence of 2,2′-bipyridyl (bipy) followed by addition of $Na[BPh_4]$ afforded, after work-up, yellow crystals of a complex which analysed (Table 1) correctly for $[In(bipy)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2][BPh_4]$, **10**. An infrared spectrum of **10** in thf is shown in Fig. 1(*g*) (Table 1) and

Table 1 Infrared and analytical[a] data for the complexes

			Analysis (%)		
	Compound	$\nu(CO)^b/cm^{-1}$	C	H	N
4a	$Na/K[InCl_2\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]$	1978m, 1955s, 1894m, 1873m, 1789w, 1746w			
7	$[InCl(thf)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$	1998s, 1976s, 1895s	33.65 (33.70)	2.40 (2.55)	
7a	$[InCl(Br)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]^-$	1991m, 1967s, 1897m, 1882m			
6	$[InCl\{W(CO)_3(\eta\text{-}C_5H_5)\}_2]$	1992s, 1970s, 1888s, 1873(sh)[c]	24.50 (23.55)	1.25 (1.25)	
5	$[InCl\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]$	1985s, 1963s, 1888s, 1873(sh)[d]	34.30 (34.80)	1.65 (1.80)	
10	$[In(bipy)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2][BPh_4]$	1989m, 1967s, 1899m, 1882m	55.55 (55.60)	3.35 (3.55)	2.60 (2.60)
12	$[InI(thf)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$	1997s, 1974s, 1896s	29.95 (29.90)	2.30 (2.25)	
13	$[InCl(py)\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]$	1983s, 1961s, 1886s, 1871m	39.50 (39.95)	2.30 (2.40)	2.15 (2.20)
14	$[InCl(py)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$	1992m, 1968s, 1895m, 1882m[e]	35.30 (35.05)	2.10 (2.10)	1.95 (1.95)
15	$[N(PPh_3)_2][InCl_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$	1985s, 1961m, 1899s, 1867m, 1783w	51.15 (51.40)	3.30 (3.30)	1.20 (1.15)
16	$[PPh_3(CH_2Ph)][InCl_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$	1987s, 1963m, 1899s, 1869m, 1781w			
17	$[NMe_4][InCl_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$	1987m, 1963s, 1892s	33.00 (32.05)	2.90 (2.95)	1.40 (1.85)
18	$[NEt_4][InI_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$	1987s, 1963s, 1894s, 1877(sh)	28.65 (29.15)	2.85 (3.05)	1.20 (1.40)
19	$[N(PPh_3)_2][InCl_2\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]$	1974s, 1950m, 1894s, 1860m, 1779m	55.90 (55.45)	3.55 (3.60)	1.20 (1.25)
20	$[PPh_3(CH_2Ph)][InCl_2\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]$	1975s, 1951m, 1891s, 1863m, 1781w			
21	$[NMe_4][InCl_2\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]$	1976s, 1953s, 1892s, 1766m	36.10 (36.30)	3.30 (3.35)	2.10 (2.10)
24	$Na[InCl_3\{Cr(CO)_3(\eta\text{-}C_5H_5)\}]$	1991s, 1924m, 1899s			
25	$Na[InI_3\{Mo(CO)_3(\eta\text{-}C_5H_5)\}]$	1985s, 1899s			
26	$[InCl_2\{Mo(CO)_3(\eta\text{-}C_5H_4Me)\}]$	2003s, 1931m, 1909s			
27	$[InCl_2\{Mo(CO)(dppe)(\eta\text{-}C_5H_5)\}]$	1836			
28	$[In\{Mo(CO)_2(CNBu^t)(\eta\text{-}C_5H_5)\}_3]$	1919s, 1879(sh), 1856s[f]			
29	$[In\{Mo(CO)_2[P(C_6H_4Me\text{-}p)_3](\eta\text{-}C_5H_5)\}_3]$	1899m, 1880m, 1837s, 1824s			

[a] Calculated values are given in parentheses. [b] Measured in thf solution. [c] These data are for the thf adduct **8**, see text. [d] These data are for the thf adduct **9**, see text. [e] These data are for the halide adduct **14a**, see text. [f] ν(CN) 2104 and 2063 cm⁻¹.



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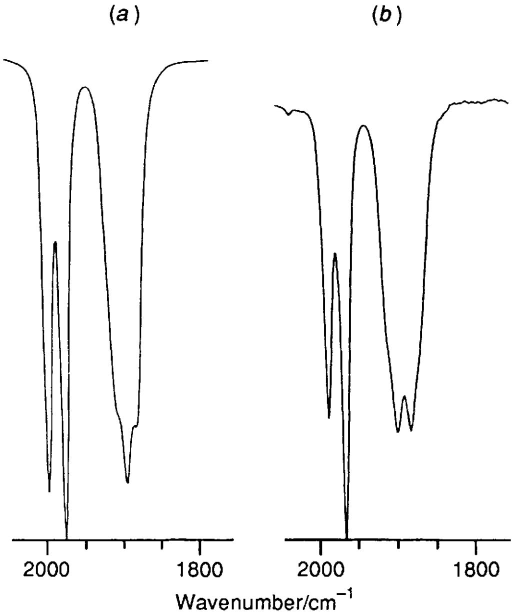


Fig. 2 Solution infrared spectra of complex **12** in the carbonyl stretching region in thf: (*a*) in CaF_2; (*b*) in KBr

the similarity to the spectrum of **7a**, shown in Fig. 1(*c*), is clear. This indicates that the $InMo_2$ fragments in **10** and **7a** are very similar, and provides further support for the structures of **7a** and **9a**.

At this stage we will mention a number of reactions which we have carried out using indium bromides and iodides. Indium monoiodide reacts with $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ in toluene and affords $[InI\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ **11**, as a yellow powder. Crystallisation from thf–hexane mixtures afforded yellow crystals of $[InI(thf)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ **12**, analytical data for which are given in Table 1 and NMR data in Table 2. As with the chloride system, two distinct infrared spectra were obtained in thf depending on the type of cells used which are shown in Fig. 2(*a*) (CaF_2) and (*b*) (KBr). The spectrum in Fig. 2(*a*) is assigned to $[InI(thf)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$, *i.e.* **12**, but that in Fig. 2(*b*) is identical to that of **7a**, *i.e.* in Fig. 1(*c*), and is therefore assumed to be due to a dihalogeno anionic complex, presumably $[InI(Br)\{Mo(CO)_3(\eta\text{-}C_5H_5)_2\}]^-$. The reaction between InI_3 and 2 equivalents of $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$ afforded a yellow solid which, upon dissolution in thf, gave an infrared spectrum (in CaF_2) identical to that of **12** [Fig. 2(*a*)]. We note the contrast with the chloride system since the analogous reaction between $InCl_3$ and $2Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$ afforded **1a**[2] rather than **7**.

We will now turn to an aspect of the chemistry of the monochloride species $[InCl\{M(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (M = Cr, **5**; or Mo, **3**) namely their interaction with Lewis bases. We have already seen that both complexes form adducts with chloride, *i.e.* **4a** and **1a** respectively, and also that thf is readily complexed, *e.g.* **7**. It is unlikely that **5** and **3** exist as monomers at all (see above) and we have been able to exploit this factor in carrying out further studies. Thus **5** and **3** readily form adducts with pyridine (py), $[InCl(py)\{M(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (M = Cr, **13**; or Mo, **14**). Both complexes were characterised by ^1H NMR spectroscopy (Table 2) and elemental analysis (Table 1) and, in the case of **13**, by an X-ray crystal-structure determination, the details of which are presented and described in the following section. Infrared spectra in thf for **13** and **14** are shown in Fig. 3(*a*) (CaF_2) and (*b*) (KBr) respectively and indicate, on the basis of what we have said before, that halide abstraction occurs in KBr cells. Thus the data for **14** in Table 1 and Fig. 3(*b*) are for the halide adduct **14a** analogous to **7a**.

We have also examined adducts with chloride in more detail.

Table 2 Proton and ^{13}C-{^{1}H} NMR data for the complexes[a]

Compound	^{1}H(δ)[b]	^{13}C(δ)[b,c]
7	5.59 (s, 10 H, C_5H_5)	91.0 (C_5H_5)
	3.63 (m, 4 H, thf)	68.2 (thf)
	1.78 (m, 4 H, thf)	26.2 (thf)
6	5.70 (C_5H_5)	89.8 (C_5H_5)
5	5.12 (C_5H_5)	87.5 (C_5H_5)
12	5.59 (s, 10 H, C_5H_5)	91.9 (C_5H_5)
	3.63 (m, 4 H, thf)	68.1 (thf)
	1.79 (m, 4 H, thf)	26.1 (thf)
13	8.92 (d, 2 H, py)	
	8.15 (t, 1 H, py)	
	7.75 (m, 2 H, py)	
	5.08 (s, 10 H, C_5H_5)	
14[d]	8.91 (d, 2 H, py)	
	8.05 (t, 1 H, py)	
	7.65 (m, 2 H, py)	
	5.41 (s, 10 H, C_5H_5)	
15	7.53 –7.80 [m, 30 H, $N(PPh_3)_2$]	
	5.47 (s, 10 H, C_5H_5)	
17	5.49 (s, 10 H, C_5H_5)	90.8 (C_5H_5)
	3.44 (s, 12 H, NMe_4)	55.9 (NMe_4)
18	5.50 (s, 10 H, C_5H_5)	92.8 (C_5H_5)
	3.50 (q, 8 H, NCH_2CH_3, $^3J_{HH}$ = 7.3 Hz)	53.0 (NCH_2CH_3)
	1.40 (tt, 12 H, NCH_2CH_3, $^3J_{HH}$ = 7.3, $^3J_{NH}$ = 1.9 Hz),	7.7 (NCH_2CH_3)
19	7.53 –7.79 [m, 30 H, $N(PPh_3)_2$]	
	5.01 (s, 10 H, C_5H_5)	
21	5.02 (s, 10 H, C_5H_5)	
	3.44 (s, 12 H, NMe_4)	
24	5.18 (s, C_5H_5)	86.7 (C_5H_5)
	3.65 (m, thf)	68.2 (thf)
	1.79 (m, thf)	26.1 (thf)
25	5.45 (s, C_5H_5)	92.1 (C_5H_5)
	3.62 (m, thf)	
	1.77 (m, thf)	
28[d]	5.30 (s, 15 H, C_5H_5)	88.7 (C_5H_5)
	1.44 (s, 27 H, $CNBu^t$)	31.8 ($CNBu^t$)
29[d,e]	7.15 –7.61 (m, 12 H, C_6H_4Me)	210 (CO)
		129.0, 122.9, 119.2 (C_6H_4Me)
	5.01 (s, 15 H, C_5H_5)	85.9 (C_5H_5)
	2.34 (s, 9 H, C_6H_4Me)	26.4 (C_6H_4Me)

[a] Chemical shifts in ppm, measurements at room temperature. [b] Measured in $(CD_3)_2CO$ unless otherwise stated. [c] ^{1}H Decoupled, chemical shifts are positive to high frequency of $SiMe_4$. [d] Measured in CD_2Cl_2. [e] ^{31}P-{^{1}H} δ 67.6 (H_3PO_4).

For the molybdenum complexes the structure of **1a** is reported in ref. 2 and we have already described the infrared spectrum in thf which is identical to that of **7a** [Fig. 1(*c*)]. The reaction between **7** and 1 equivalent of $[N(PPh_3)_2]Cl$, $[PPh_3(CH_2Ph)]Cl$ or $[NMe_4]Cl$ in thf afforded, after work-up and crystallisation, the yellow crystalline complexes, $[Q][InCl_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ [Q = $N(PPh_3)_2$, **15**; $PPh_3(CH_2Ph)$, **16**; or NMe_4, **17**]. Solution infrared spectra in thf are shown in Fig. 3(*c*), (*d*) and (*e*) respectively (numerical data in Table 1). The spectra for **15** and **16** are clearly very similar yet different to either that of **7** or **1a**, moreover the weak absorptions at ≈1780 cm^{-1} are indicative of a small degree of dissociation of $[Mo(CO)_3(\eta\text{-}C_5H_5)]^-$. Clearly a mixture of at least two species is present in solution but it is difficult to be more precise about the exact nature of these compounds. Not only is the situation complicated by dissociation but the problem of significant ion-pairing interactions must also be considered. We have come across this before in related indium chemistry involving the $Fe(CO)_2(\eta\text{-}C_5H_5)$ fragment[5] where a change in the cation, Q^+, often leads to quite different-looking spectra. This is again obvious if we look at the spectrum of complex **17** [Fig. 3(*e*)] which is different from those for **15** and **16**. Compound **17** was structurally characterised by X-ray crystallography and details are given in the next section but, as we shall see, the $[InCl_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]^-$ units in **17** and **1a** are different with respect to the relative orientations of the $Mo(CO)_3(\eta\text{-}C_5H_5)$ fragments and the $InCl_2$ group. If such structural differences are maintained in solution as a result of significant ion pairing, then this would account, at least in part, for the different spectra observed.

The iodide complex $[NEt_4][InI_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ **18** is clearly very similar to **17** on the basis of the infrared spectra observed [Fig. 3(*f*) *vs.* (*e*)] and the chromium complexes are also similar, in most respects, to the molybdenum compounds just described. Thus the reactions between **9** and QCl afforded the complexes $[Q][InCl_2\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]$ [Q = $N(PPh_3)_2$, **19**; $PPh_3(CH_2Ph)$, **20**; or NMe_4, **21**] spectra for which are shown in Fig. 3(*g*), (*h*) and (*i*) respectively. These are clearly similar to the corresponding spectra for the molybdenum compounds with the exception that the low-frequency absorptions due to $[Cr(CO)_3(\eta\text{-}C_5H_5)]^-$ are more intense which indicates that dissociation is more extensive.

In concluding this section we shall mention the results from a few experiments which are of relevance to our overall theme. In ref. 2 we reported details of the reactions between $InCl_3$ and 1 equivalent of either $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$ or $Na[W(CO)_3(\eta\text{-}C_5H_5)]$ which afforded the anionic complexes $[InCl_3\{M(CO)_3(\eta\text{-}C_5H_5)\}]^-$ (M = Mo, **22**; or W, **23**). Compound **22** was found to be $[Na(thf)_2][InCl_3\{Mo(CO)_3(\eta\text{-}C_5H_5)\}]$ **22a**, in the solid state by X-ray crystallography.[2] The analogous chromium reaction proceeded similarly and afforded a complex identified as $Na[InCl_3\{Cr(CO)_3(\eta\text{-}C_5H_5)\}]$ **24**, on the basis of the similarity of the infrared spectrum [Fig. 4(*a*)] to that observed for **22** [Fig. 6(*a*) in ref. 2]. The reaction between InI_3 and $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$ afforded the analogous iodide complex $Na[InI_3\{Mo(CO)_3(\eta\text{-}C_5H_5)\}]$ **25** [Fig. 4(*b*)]. According to Hsieh and Mays[4] neutral complexes of the form $[InX_2\{M(CO)_3(\eta\text{-}C_5H_5)\}]$ can be made directly from the reaction between $[MX(CO)_3(\eta\text{-}C_5H_5)]$ and InX. We carried out two similar reactions, *viz.* InCl with $[MoCl(CO)_3(\eta\text{-}C_5H_4Me)]$ and InCl with $[MoCl(CO)(dppe)(\eta\text{-}C_5H_5)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) which afforded complexes which we propose to be $[InCl_2\{Mo(CO)_3(\eta\text{-}C_5H_4Me)\}]$ **26** and $[InCl_2\{Mo(CO)(dppe)(\eta\text{-}C_5H_5)\}]$ **27**, respectively. Infrared data are given in Table 1 and, for **26**, in Fig. 4(*c*), but both compounds were difficult to purify and crystallise and we will not comment further on these reactions or the precise nature of the species formed.

The trimolybdenum species $[In\{Mo(CO)_2L(\eta\text{-}C_5H_5)\}_3]$ [L = $CNBu^t$, **28**; or $P(C_6H_4Me\text{-}p)_3$, **29**] were synthesised from the reactions between $InCl_3$ and $3Na[Mo(CO)_2L(\eta\text{-}C_5H_5)]$; data for them are given in Tables 1 and 2 and Fig. 4(*d*) and (*e*). We were not able to obtain crystals suitable for X-ray diffraction studies so we cannot be certain as to the structures.

The complex $[In\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$ reacted with 0.5 equivalent of $InCl_3$ in thf according to equation (1) and provides an alternative synthetic route to **7**.

$$2[In\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3] + InCl_3 \xrightarrow{\text{thf}} 3[InCl(thf)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2] \quad (1)$$

Finally we mention some reactions which are of interest with respect to a recent paper by Ziegler and co-workers[7] and which we described in a footnote to a preliminary communication.[3] Ziegler and co-workers described the reaction between $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ and $InCl_3$ in diglyme (2,5,8-trioxanonane) which afforded as one product, the ionic material $[Mo_3(CO)_6O(\eta\text{-}C_5H_5)_3][InCl_3\{Mo(CO)_3(\eta\text{-}C_5H_5)\}]$, *i.e.* containing the same anion as **22**. We have studied the reactions between $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ (Mo≡Mo) in refluxing toluene with either $InCl_3$ or InCl. The former reaction afforded a product **30**,

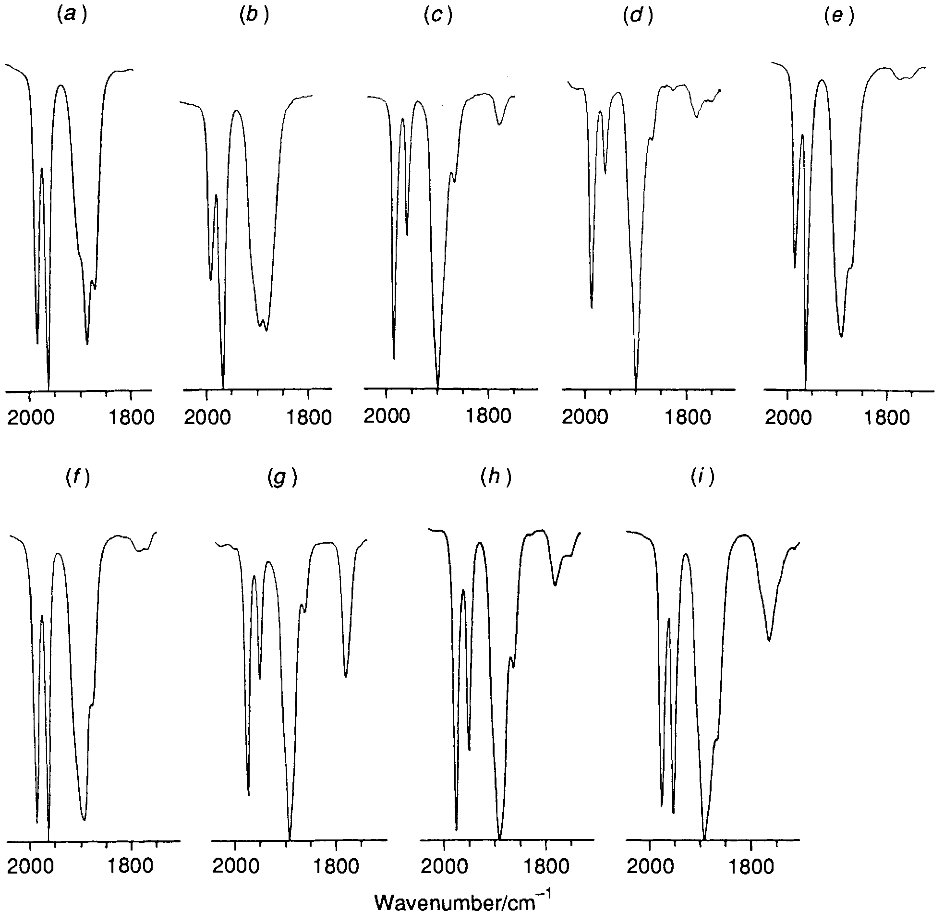
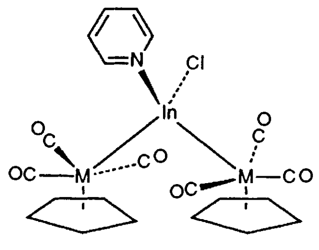
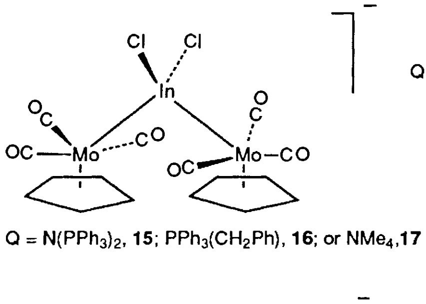


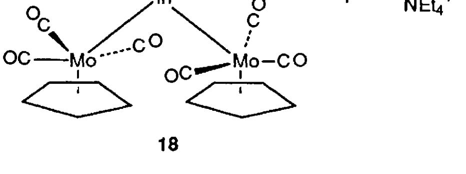
Fig. 3 Solution infrared spectra in the carbonyl stretching region in thf in CaF_2 cells: (*a*) complex **13**, (*b*) **14a** run in KBr cells, (*c*) **15**, (*d*) **16**, (*e*) **17**, (*f*) **18**, (*g*) **19**, (*h*) **20** and (*i*) **21**



M = Cr, **13**; or Mo, **14**



Q = $N(PPh_3)_2$, **15**; $PPh_3(CH_2Ph)$, **16**; or NMe_4,**17**



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an infrared spectrum of which is shown in Fig. 4(*f*), whilst the latter reaction gave a product **31** the spectrum of which is shown in Fig. 4(*g*). The resemblance between Figs. 4(*f*) and 3(*e*) is noteworthy as is that between Fig. 4(*g*) and Fig. 3(*c*) and (*d*). This therefore indicates that the anion $[InCl_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]^-$ is probably formed in the above two reactions but we will not speculate on the nature of the cation.

Having considered the solution-state properties of many of the complexes described in this section we will now turn to the solid-state structures.

(*ii*) *Structures*.—A view of the structure of complex **7** is shown in Fig. 5, selected bond distance and angle data are given in Table 3 and atomic positional parameters in Table 4. The structure is best described as containing a four-co-ordinate, tetrahedral indium centre bonded to two $Mo(CO)_3(\eta\text{-}C_5H_5)$ fragments, a chlorine atom and a thf molecule. All of these groups have normal geometries and the In–Mo bond lengths [2.814(1) and 2.835(1) Å] have already been mentioned and compared with other such bonds in the preceding paper.[1] What concerns us here are the interbond angles around the indium centre. Specifically there are two angles which differ markedly from ideal tetrahedral values, *viz*. Mo(1)–In–Mo(2) 128.2(1) and Cl–In–O(7) 92.5(2)°, and, as we shall see, this situation is quite general.

The structure of complex **13** is shown in Fig. 6 with relevant metric parameters in Tables 5 and 6. The overall molecular structure is very similar to **7**; the In–Cr bond lengths are 2.760(1) and 2.785(1) Å, which are comparable with the values found for $[In\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_3]$ [2.806(1), 2.801(1) and 2.775(1) Å] and $[InBr(thf)\{Cr(CO)_5\}]$ [2.554(3) and 2.562(3) Å] (see

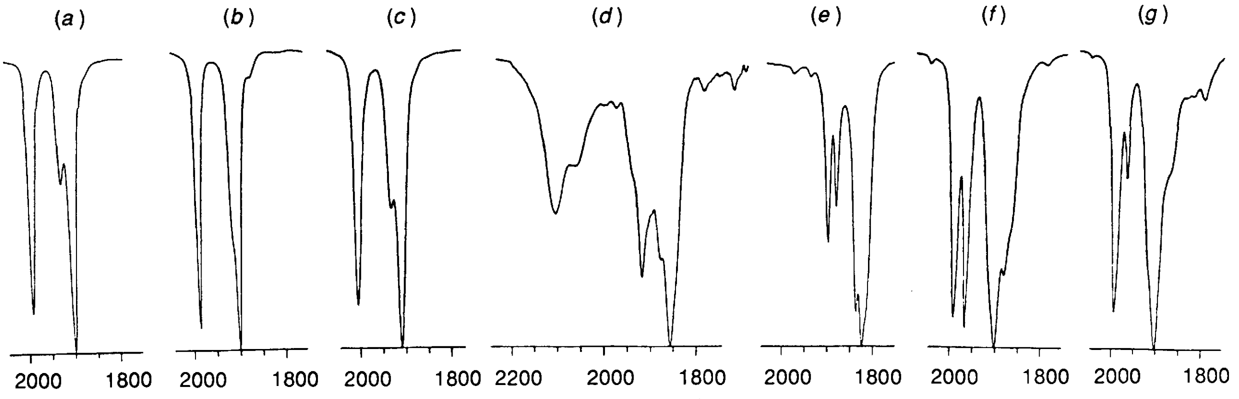

Fig. 4 Solution infrared spectra in the carbonyl stretching region in thf in CaF_2 cells: (*a*) complex **24**, (*b*) **25**, (*c*) **26**, (*d*) **28**, (*e*) **29**, (*f*) **30** [ν(CO) 1992s, 1968s, 1903s and 1884(sh)] and (*g*) **31** [ν(CO) 1994s, 1968m, 1903s and 1798w cm^{-1}]

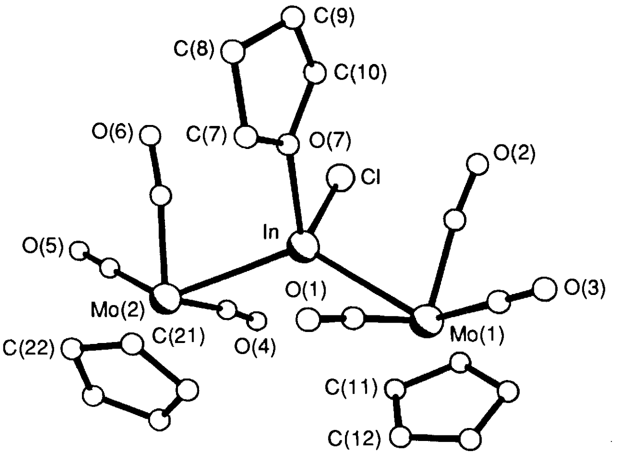

Fig. 5 A view of the molecular structure of complex **7** showing the atom numbering scheme. Hydrogen atoms omitted for clarity

Table 3 Selected bond lengths (Å) and angles (°) for complex **7**

In–Mo(1)	2.814(1)	In–Mo(2)	2.835(1)
In–Cl	2.437(2)	In–O(7)	2.301(5)
Mo(1)–In–Mo(2)	128.2(1)	Mo(1)–In–Cl	109.3(1)
Mo(1)–In–O(7)	104.0(2)	Mo(2)–In–Cl	110.5(1)
Mo(2)–In–O(7)	106.1(2)	Cl–In–O(7)	92.5(2)

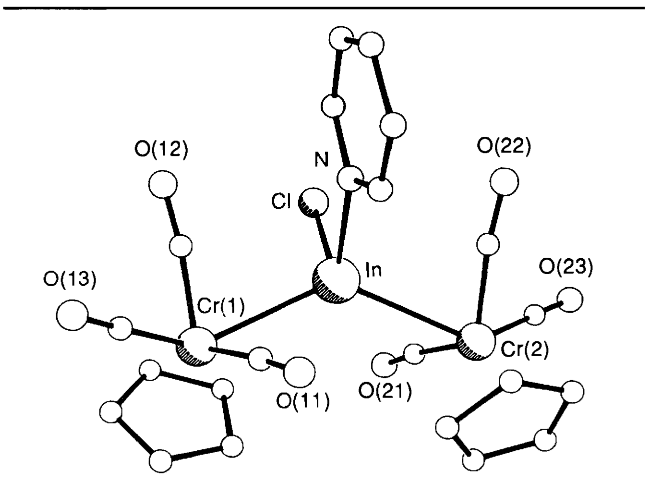

Fig. 6 A view of the molecular structure of complex **13** showing the atom numbering scheme. Hydrogen atoms omitted for clarity

preceding paper[1]), and the relevant angles about the indium centre are Cr(1)–In–Cr(2) 130.1(1) and Cl–In–N 95.1(2)°.

Finally, the structure of complex **17** (not including the $[NMe_4]^+$ cation) is shown in Fig. 7; metric parameters are given in Tables 7 and 8. Again, the structure is very similar to **7** with a In–Mo bond length of 2.857(1) Å and angles Mo–In–Mo′ 126.2(1) and Cl–In–Cl′ 99.4(1)°. It is instructive to compare this structure to that of **1a**.[2] They differ in the nature of the cation, $[NMe_4]^+$ for **17**, $[Na(thf)_2]^+$ for **1a**, but it is apparent when comparing the view of the anion $[InCl_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]^-$ in **17** (Fig. 7) with that in **1a** (Fig. 8) that the precise structures are different, specifically the conformations about the In–Mo bonds. These are best measured by the torsion angles defined as Cl,Cl midpoint–In–Mo–C_5H_5 ring centroid. For **17** this angle is 129.5° for both In–Mo bonds since the molecule lies on a crystallographic C_2 axis whilst for **1a** the values are −23.1 for Mo(1) and 98.2° for Mo(2). Clearly the differences between **17** and **1a** are likely to arise as a result of having different cations and therefore corresponding differences in steric and crystal-packing forces. It is possible, however, that some conformations are preferred for electronic reasons, a point to which we shall return in a moment.

Returning to the angles about indium, the two of most importance in complex **1a** are Mo(1)–In–Mo(2) 129.4(1) and Cl(1)–In–Cl(2) 90.4(1)°,[2] quite similar to those in **17**. So far, the range we have seen for the M–In–M angles is 126.2–130.1° whilst that for the angle which we shall denote as X–In–X (X = Cl, O or N) is 90.4–99.4°. In a recent paper reporting results on indium complexes containing the $Fe(CO)_2(\eta\text{-}C_5H_5)$ fragment[5] we drew attention to related angles of similar magnitude in the complexes $[\{InCl[Fe(CO)_2(\eta\text{-}C_5H_5)]_2\}_2]$ [131.5(1) and 80.0(1)°],[5] $[InCl(PMe_2Ph)\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ [124.8(1) and 89.0(1)°],[5] six complexes of general formula $[\{InX[M(CO)_5]_2\}_2]$ (X = Cl, Br or I; M = Mn or Re) (M–In–M 123.6–128.4°, X–In–X 80.0–97.2°),[6] $[N(PPh_3)_2][InCl_2\{Co(CO)_4\}_2]$ (av. 121.9 and 102.4°),[8] $[Co(CO)_3(PPh_3)_2][InCl_2\{Co(CO)_4\}_2]$ [121.5(1) and 102.5(1)°],[8] and $[NEt_4][InBr_2\{Co(CO)_4\}_2]$ [124.3(4) and 103.5(3)°].[9] As we can see, the range of values for the M–In–M angle is only 121.5–130.1°; that for X–In–X is 80.0–103.5° but the larger range found here reflects the fact that the neutral monochloride complexes exist as dimers and contain a In_2Cl_2 ring. This doubtless constrains the angles in these cases to some extent.

It is also instructive to compare the indium compounds described above to some related and formally isoelectronic tin complexes. Thus, structures have been reported for compounds of the general form $[SnCl_2(ML_n)_2]$ for ML_n = $Co(CO)_4$,[10] $Co(CO)_2(nbd)$ (nbd = norbornadiene),[11] $Fe(CO)_2(\eta\text{-}C_5H_5)$,[12] $Mn(CO)_5$,[13] and $Cr(CO)_3(\eta\text{-}C_5H_5)$[14] and for these five complexes the M–Sn–M angles are 129.3(1), 128.3(1), 128.6(3), 126.2(1) and 130.2(1)° and the Cl–Sn–Cl angles are 101.3(1), 98.1(1), 94.1(6), 95.8(1) and 95.0(1)° respectively, *i.e.* a similar range of angles. In particular, it is informative to look at the

Table 4 Atomic coordinates (× 10^4) for complex **7**

Atom	*x*	*y*	*z*
In	6764.4(3)	1585.2(4)	2428.6(2)
Mo(1)	6085.4(4)	−1308.4(5)	2258.4(3)
Mo(2)	8299.1(3)	2714.5(6)	3682.2(3)
Cl	5550(1)	3344(2)	2120(1)
O(1)	7901(4)	−1534(6)	2028(4)
O(2)	4779(4)	512(6)	794(3)
O(3)	5709(4)	−3527(6)	785(3)
O(4)	6762(3)	3112(7)	4323(3)
O(5)	8614(5)	5923(6)	4349(4)
O(6)	7917(4)	4716(6)	2112(3)
O(7)	6940(3)	2034(5)	1184(3)
C(1)	7224(5)	−1386(7)	2113(4)
C(2)	5306(4)	−109(7)	1333(4)
C(3)	5851(5)	−2724(7)	1325(4)
C(4)	7295(5)	2980(8)	4040(4)
C(5)	8498(5)	4731(8)	4103(5)
C(6)	8011(5)	3915(8)	2654(5)
C(7)	7669(9)	1632(11)	957(6)
C(8)	7608(10)	2461(18)	213(7)
C(9)	6709(10)	2848(16)	−139(6)
C(10)	6325(7)	2847(12)	500(5)
C(11)	6119(8)	−788(10)	3593(5)
C(12)	6565(5)	−2054(11)	3641(4)
C(13)	6017(9)	−3089(8)	3187(6)
C(14)	5191(8)	−2472(18)	2842(6)
C(15)	5262(9)	−1043(15)	3101(8)
C(21)	9278(8)	984(13)	3505(5)
C(22)	9763(5)	2056(12)	4069(9)
C(23)	9536(6)	1917(11)	4753(6)
C(24)	8948(6)	829(10)	4635(5)
C(25)	8761(5)	257(8)	3877(6)

Table 5 Selected bond lengths (Å) and angles (°) for complex **13**

In–Cr(1)	2.760(1)	In–Cr(2)	2.785(1)
In–Cl	2.456(2)	In–N	2.335(5)
Cr(1)–In–Cr(2)	130.1(1)	Cr(1)–In–Cl	107.6(1)
Cr(1)–In–N	103.6(2)	Cr(2)–In–Cl	107.3(1)
Cr(2)–In–N	107.6(1)	Cl–In–N	95.1(2)

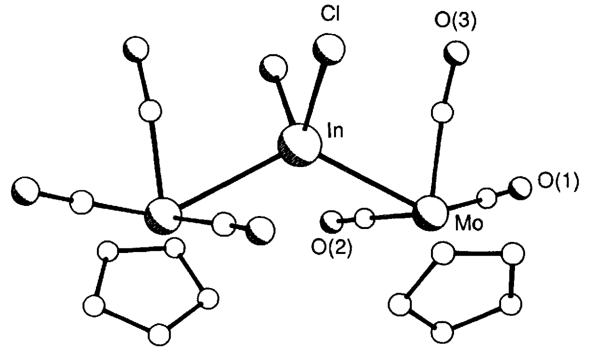

Fig. 7 A view of the molecular structure of the anion $[InCl_2\{Mo(CO)_3(\eta-C_5H_5)\}_2]^-$ of **17** showing the atom numbering scheme. Hydrogen atoms omitted for clarity

Table 6 Atomic coordinates (× 10^4) for complex **13**

Atom	*x*	*y*	*z*
In	1254.8(6)	1333.6(6)	2614.2(3)
Cr(1)	−22.8(12)	−1697.4(12)	2774.9(6)
Cr(2)	2991.3(12)	2630.4(13)	1345.8(6)
Cl	−944(2)	2892(2)	2928(1)
N	2867(7)	2124(7)	3865(3)
C(1)	2299(9)	2951(9)	4482(4)
C(2)	3253(13)	3395(11)	5220(5)
C(3)	4828(12)	3014(12)	5320(6)
C(4)	5415(13)	2207(12)	4676(7)
C(5)	4404(11)	1782(11)	3971(6)
C(11)	2258(9)	−1496(8)	2824(5)
O(11)	3696(6)	−1506(7)	2853(4)
C(12)	−641(9)	−487(8)	3663(5)
O(12)	−1137(8)	141(7)	4232(3)
C(13)	391(9)	−2907(9)	3627(5)
O(13)	735(8)	−3612(7)	4155(4)
C(14)	−2597(10)	−2102(13)	2224(6)
C(15)	−2085(11)	−3493(10)	2286(6)
C(16)	−781(10)	−3590(9)	1804(5)
C(17)	−444(11)	−2232(13)	1427(5)
C(18)	−1617(13)	−1281(11)	1692(6)
C(21)	741(8)	2226(9)	1020(4)
O(21)	−620(7)	2023(8)	731(3)
C(22)	3423(9)	3931(9)	2308(4)
O(22)	3811(9)	4858(7)	2863(4)
C(23)	2778(11)	4468(13)	940(6)
O(23)	2643(11)	5622(10)	670(6)
C(24)	3461(10)	796(11)	436(6)
C(25)	3990(12)	430(11)	1201(6)
C(26)	5281(12)	1638(16)	1526(6)
C(27)	5497(10)	2691(13)	915(7)
C(28)	4359(12)	2129(12)	257(5)

Table 7 Selected bond lengths (Å) and angles (°) for complex **17**

In–Mo	2.857(1)	In–Cl	2.478(3)
Mo–In–Mo′	126.2(1)	Mo–In–Cl	106.4(1)
Mo–In–Cl′	107.7(1)	Cl–In–Cl′	99.4(1)

Table 8 Atomic coordinates (× 10^4) for complex **17**

Atom	*x*	*y*	*z*
In	0.0	7254.0(8)	2500.0
Mo	−1365.9(5)	6325.9(7)	2605.5(9)
Cl	−546(2)	8405(3)	709(3)
O(1)	−2273(8)	6661(9)	4290(10)
O(2)	−46(5)	6181(7)	5313(9)
O(3)	−1670(6)	8513(8)	2410(10)
C(1)	−1913(8)	6520(10)	3680(20)
C(2)	−461(7)	6240(8)	4290(10)
C(3)	−1512(8)	7700(10)	2500(10)
C(11)	−2364(9)	5820(10)	650(20)
C(12)	−2290(10)	5120(20)	1580(20)
C(13)	−1530(20)	4740(10)	2040(20)
C(14)	−1160(10)	5170(20)	1340(30)
C(15)	−1670(10)	5850(20)	520(20)
N	5290(10)	6190(20)	2850(20)
C(20)	5660(10)	5600(20)	2310(20)
C(21A)	4300(20)	6180(30)	870(40)
C(21B)	5360(20)	7220(30)	2430(50)

structure of $[SnCl_2\{Cr(CO)_3(\eta-C_5H_5)\}_2]$[14] **32**, in a little more detail because of the obvious similarity to **1a** and **17**. A view of the molecular structure of **32** is shown in Fig. 9 and the relevant torsion angles, defined as before, are −12.0 and 99.0°, very close to those found in **1a**.

If we concentrate on the M–In/Sn–M angles (av. M–In–M 126.3, av. M–Sn–M 128.5°), it is tempting to ascribe the increase over and above the tetrahedral angle of 109.5° to steric factors resulting from the large ML_n fragments. We draw attention, however, to a series of four bismuth complexes, which we have recently prepared, of the form $[BiCl_2(ML_n)_2]^-$ which have much smaller M–Bi–M angles. Specifically, for the complexes $[N(PPh_3)_2][BiCl_2\{Fe(CO)_2(\eta-C_5H_5)\}_2]$,[15] $[N(PPh_3)_2][BiCl_2\{Mo(CO)_3(\eta-C_5H_5)\}_2]$,[15] $[PPh_3(CH_2Ph)][BiCl_2\{Mo(CO)_3(\eta-C_5H_5)\}_2]$[16] and $[N(PPh_3)_2][BiCl_2\{W(CO)_3(\eta-C_5H_5)\}_2]$,[16] the M–Bi–M angles are 111.4(1), 116.4(1), 117.0(1) and 116.2(1)° (av. 115.3°) whilst the Cl–Bi–Cl angles are 155.6(2), 138.5(1), 154.7(1) and 139.8(2)° respectively (av.

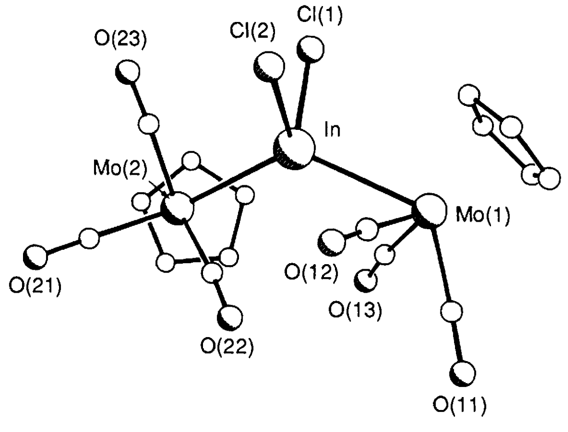

Fig. 8 A view of the anion $[InCl_2\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]^-$ from the structure of **1a** redrawn with coordinates from ref. 2

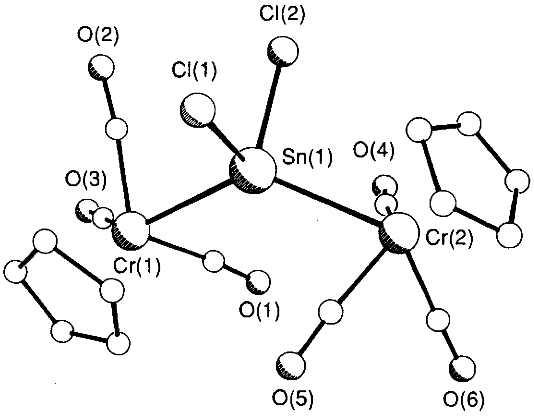

Fig. 9 A view of the molecular structure of complex **32** redrawn with coordinates from ref. 14

147.2°). In ref. 15 we considered the possibility that the Cl–Bi–Cl angle is influenced by electronic factors, in particular transition metal π to Cl–Bi–Cl σ^* negative hyperconjugation, but it is apparent that, as a general rule, the indium and tin complexes have larger angles between the metals and smaller angles between the chlorines than do the bismuth compounds. We suspect that, although steric factors have a role to play, this difference is partly electronic in origin and reflects the addition of two extra valence electrons in going from the In/Sn systems to the bismuth compounds. We shall return to this matter in considerably more detail in a future publication in which we shall attempt to study any electronic factors with the aid of extended-Hückel molecular orbital calculations. We note at this time, however, that a simple electronic argument for the structure of $[SnCl_2\{Co(CO)_4\}_2]$ has been presented by Mackay *et al.*[10] based on the hybridisation at tin which results from the differing electronegativities of the Cl and $Co(CO)_4$ fragments, an application of Bent's rule in fact.[17]

Finally we draw attention to a further structural relationship. In ref. 5 we commented on the similarity of the structures of $[InCl\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2]$ and $[BiCl\{Mn(CO)_2(\eta\text{-}C_5H_5)\}_2]$; both are chloro-bridged dimers and, with respect to their valence electrons, are isoelectronic. 'Inidene' complexes of the lighter Group 15 elements, *i.e.* P, As and Sb, are monomeric and have been studied in great detail by Huttner and co-workers,[18] but in all cases these compounds exhibit Lewis acidity at the Group 15 element centre. This aspect of their reactivity has been mentioned in detail in ref. 18, and refs. therein, but we note a recent report by Huttner and co-workers[19] on the synthesis and structure of the anionic complexes $[AsCl_2\{Cr(CO)_5\}_2]^-$ and $[SbCl_2\{Mn(CO)_2(\eta\text{-}C_5H_4Me)\}_2]^-$. Both of these complexes are formally isoelectronic with species of general formula $[InCl_2(ML_n)_2]^-$ and $[SnCl_2(ML_n)_2]$ where ML_n is a 17-electron fragment. For the former complex, the relevant angles, with respect to our foregoing discussion, are Cr–As–Cr 131.1(1) and Cl–As–Cl 92.6(1)° and for the latter are Mn–Sb–Mn 134.4(1) and Cl–Sb–Cl 93.4(1)°, *i.e.* very similar to the corresponding angles in the indium and tin complexes.

Experimental

General Considerations.—All reactions were performed using standard Schlenk techniques under an atmosphere of dry, oxygen-free dinitrogen. All solvents were distilled from appropriate drying agents (sodium–benzophenone for thf, Et_2O, hexane and toluene; CaH_2 for CH_2Cl_2 and MeCN) immediately prior to use. Infrared spectra were recorded on a Nicolet 20 SXB FTIR spectrometer, ^1H and ^{13}C NMR spectra on a Bruker WP 200 spectrometer operating at 200.13 and 50.324 MHz respectively in dried and degassed deuteriated solvents. Chemical shifts were referenced to residual solvent signals with values taken from ref. 20. Microanalytical data were obtained at the University of Newcastle.

All indium salts and other reagents were procured commercially and used without further purification except InI which was prepared according to Freeland and Tuck.[21] The complexes $[M_2(CO)_6(\eta\text{-}C_5H_5)_2]$ were prepared by the method of Manning and co-workers.[22]

Preparations.—$[Na/K(thf)_2][InCl_2\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]$ **4a**. A stirred solution of $Na/K[Cr(CO)_3(\eta\text{-}C_5H_5)]$, derived from NaK alloy (1:1) (0.3 cm^3) reduction of $[Cr_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (0.182 g, 0.453 mmol), in thf (10 cm^3) was cooled to 0 °C (ice-bath) and maintained at this temperature. To this was added a solution of $InCl_3$ (0.100 g, 0.453 mmol) in thf (10 cm^3) over a period of a few minutes with continuous stirring. On warming to room temperature and stirring for 1.5 h a turbid yellow solution was observed which turned green on stirring overnight. Reduction of the solvent volume by half (vacuum) followed by filtration through Celite afforded a yellow-green filtrate, from which yellow crystals were obtained after reduction of the solvent volume to 4 cm^3 and solvent diffusion of hexane (40 cm^3) at −30 °C over a period of 3 d. The crystals lost solvent rapidly on removal from the mother-liquor, washing with hexane (2 × 10 cm^3) and drying by vacuum. They would not readily dissolve in CH_2Cl_2, even on warming, and were recrystallised from thf–hexane mixtures. Two forms were apparent, large yellow-green crystals and yellow blocks, which gave identical infrared spectra in thf solution. Solvent loss was suppressed by isolating from the mother-liquor, drying briefly under a stream of dry N_2 and storing at −30 °C (yield 40% based on $InCl_3$).

This compound was also obtained, in high yield (typically 70–80% based on $InCl_3$), from reactions to prepare the trichromium–indium complex $[In\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_3]$ when the reduction of the chromium dimer $[Cr_2(CO)_6(\eta\text{-}C_5H_5)_2]$ was left for less than 5 h.

$[InCl\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ **3** *and* $[InCl(thf)\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2]$ **7**. Indium monochloride (0.148 g, 0.985 mmol) and $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (0.483 g, 0.985 mmol) were stirred in refluxing toluene (10 cm^3) for 4 h. After this time the reaction solution was cooled to room temperature and the yellow precipitate which had formed was allowed to settle. The red-brown supernatant $\{[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and unreacted $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]\}$ was syringed off, the remaining solid washed with diethyl ether until the washings were colourless (6 × 10 cm^3) and then dried by vacuum. Extraction of the yellow solid in thf (15 cm^3) followed by filtration through Celite afforded a yellow solution which, after reduction of the solvent volume to 5 cm^3 and solvent diffusion of hexane (30 cm^3) at − 30 °C over a period of 7 d, afforded a golden-yellow flaky crystalline material (yield 56–73%). Recrystallisation of a sample from thf–hexane mixtures afforded a mixture of yellow needles and dark yellow blocks which were shown to be identical by infrared spectroscopy and X-ray crystallography.

[InCl{W(CO)$_3$(η-C$_5$H$_5$)}$_2$] **6**. Indium monochloride (0.043 g, 0.288 mmol) and [W$_2$(CO)$_6$(η-C$_5$H$_5$)$_2$] (0.192 g, 0.288 mmol) were stirred in refluxing toluene (10 cm^3) for 11 h. After this time the toluene was removed by vacuum and the resulting yellow powder redissolved in thf (20 cm^3) and filtered through Celite. Reduction of the solvent volume to 7 cm^3 followed by solvent diffusion of hexane (40 cm^3) at −30 °C over a period of several days afforded yellow crystals of [InCl(thf){W(CO)$_3$(η-C$_5$H$_5$)}$_2$] **8** (yield 30%). The crystals rapidly lost solvent on removal from the mother-liquor, and after short periods under vacuum gave the thf-free product **6**.

[InCl{Cr(CO)$_3$(η-C$_5$H$_5$)}$_2$] **5**. Indium monochloride (0.183 g, 1.218 mmol) and [Cr$_2$(CO)$_6$(η-C$_5$H$_5$)$_2$] (0.490 g, 1.218 mmol) were stirred in toluene (10 cm^3) at room temperature for 48 h. (Formation of a yellow precipitate was observed after 45 min, but it took 24–48 h for the reaction to go to completion.) After this time the yellow precipitate was allowed to settle and the green supernatant {unreacted [Cr$_2$(CO)$_6$(η-C$_5$H$_5$)$_2$]} was syringed off. The solid was washed with either toluene–hexane (1:1) mixtures or diethyl ether until the washings were colourless (about 5 × 10 cm^3), and then dried by vacuum. Extraction in thf (15 cm^3) afforded a green solution from which a metallic precipitate was removed by filtration through Celite. Reduction of the solvent volume to 5 cm^3 followed by solvent diffusion of hexane (30 cm^3) at −30 °C over a period of 7 d afforded yellow blocks of [InCl(thf){Cr(CO)$_3$(η-C$_5$H$_5$)}$_2$] **9** (yield 80–85%). The crystals rapidly lost solvent on removal from the mother-liquor to give the thf-free complex **5**.

[In(bipy){Mo(CO)$_3$(η-C$_5$H$_5$)}$_2$][BPh$_4$] **10**. The compound HBF$_4$·Et$_2$O (0.012 g, 0.078 mmol) was added to a stirred solution of [In{Mo(CO)$_3$(η-C$_5$H$_5$)}$_3$] (0.066 g, 0.078 mmol) in thf (10 cm^3) at room temperature followed by 2,2′-bipyridyl (0.012 g, 0.078 mmol). The resulting yellow reaction solution was then stirred for 30 min after which time the thf was removed by vacuum affording a yellow powder. This was washed with Et$_2$O (5 × 5 cm^3), to remove [MoH(CO)$_3$(η-C$_5$H$_5$)], and then dried by vacuum, but was insoluble in CH$_2$Cl$_2$ and thf. Next a solution of Na[BPh$_4$] (0.027 g, 0.078 mmol) in MeOH–thf (1:4) (2.5 cm^3) was added to a stirred suspension of the yellow powder, obtained above, in CH$_2$Cl$_2$ (5 cm^3). After 10 min the resulting turbid dark yellow solution was filtered through Celite and the solvent volume reduced to 3 cm^3 over which hexane (20 cm^3) was layered. Solvent diffusion over a period of several days at −30 °C afforded a yellow oily residue. Successive recrystallisations from CH$_2$Cl$_2$–Et$_2$O mixtures at −30 °C afforded small yellow needles of complex **10** (yield 44%).

[InI{Mo(CO)$_3$(η-C$_5$H$_5$)}$_2$] **11** *and* [InI(thf){Mo(CO)$_3$(η-C$_5$H$_5$)}$_2$] **12**. Indium monoiodide (0.064 g, 0.265 mmol) and [Mo$_2$(CO)$_6$(η-C$_5$H$_5$)$_2$] (0.130 g, 0.265 mmol) were stirred in refluxing toluene (10 cm^3) for 2.5 h. After this time the toluene was removed by vacuum and the dark yellow residue washed with toluene–hexane (1:3) until the washings were colourless. The resulting yellow powder, **11**, was redissolved in thf (10 cm^3) and filtered through Celite. Reduction of the filtrate solvent volume to 4 cm^3 followed by solvent diffusion of hexane (30 cm^3) at −30 °C over a period of 7 d afforded small yellow crystals of [InI(thf){Mo(CO)$_3$(η-C$_5$H$_5$)}$_2$] **12** (yield 40%).

Reaction of InI$_3$ *with* 2Na[Mo(CO)$_3$(η-C$_5$H$_5$)]. A stirred solution of Na[Mo(CO)$_3$(η-C$_5$H$_5$)], derived from a Na/Hg reduction of [Mo$_2$(CO)$_6$(η-C$_5$H$_5$)$_2$] (0.131 g, 0.268 mmol) in thf (20 cm^3), was cooled to 0 °C (ice-bath) and maintained at this temperature. To this was added a solution of InI$_3$ (0.133 g, 0.268 mmol) in thf (10 cm^3). During the addition an increase in the intensity of the yellow colour and in the turbidity of the solution were observed. The solution was allowed to warm to room temperature and stirring was continued for 12 h. After this time the thf was removed by vacuum and the residue extracted in Et$_2$O (20 cm^3). Filtration through Celite followed by removal of the Et$_2$O by vacuum afforded an oily yellow residue which completely redissolved in Et$_2$O (6 cm^3). Crystallisation by solvent diffusion using hexane (30 cm^3) at −30 °C resulted in the precipitation of a yellow oil. This oil was stirred in hexane (20 cm^3) for 15 min. The pale pink hexane layer was syringed off and the resulting yellow powder dried under vacuum. This powder did not readily redissolve in Et$_2$O or CH$_2$Cl$_2$. Recrystallisation by solvent diffusion from thf–hexane mixtures at −30 °C afforded a yellow oily, semicrystalline solid which was isolated from the mother-liquor, washed with hexane (2 × 10 cm^3) and dried by vacuum (yield 0.173 g). Subsequent attempts to recrystallise the solid were unsuccessful, affording only oily residues.

[InCl(py){M(CO)$_3$(η-C$_5$H$_5$)}$_2$] (M = Cr, **13**; *or* Mo, **14**). Complex **9** or **7** was stirred with 1 equivalent of pyridine in thf (4 cm^3) for about 5 min. Recrystallisation by solvent diffusion from CH$_2$Cl$_2$–hexane mixtures at −30 °C over a period of 3–5 d afforded crystals of the pyridine adducts **13** and **14** in essentially quantitative yields. The crystals of **13** were suitable for X-ray diffraction.

[N(PPh$_3$)$_2$][InCl$_2${Mo(CO)$_3$(η-C$_5$H$_5$)}$_2$] **15**. A solution of Na[InCl$_2${Mo(CO)$_3$(η-C$_5$H$_5$)}$_2$] in thf (20 cm^3) was prepared as previously described[2] from InCl$_3$ (0.054 g, 0.244 mmol) and [Mo$_2$(CO)$_6$(η-C$_5$H$_5$)$_2$] (0.119 g, 0.244 mmol). The thf was removed by vacuum and the residue extracted in CH$_2$Cl$_2$ (20 cm^3) and filtered through Celite. A solution of [N(PPh$_3$)$_2$]Cl (0.140 g, 0.244 mmol) in CH$_2$Cl$_2$ (5 cm^3) was then added to the yellow filtrate and the reaction solution was stirred for 16 h. A small amount of solid precipitated which was removed by refiltration through Celite. The filtrate solvent volume was reduced by vacuum to 5 cm^3, over which hexane (30 cm^3) was layered. Solvent diffusion over a period of 3 d at −30 °C afforded a brown oil and a colourless mother-liquor. The brown oil was stirred in hexane (10 cm^3) for 10 min and then the hexane was syringed off and the resulting brown powder dried by vacuum. Successive recrystallisations from CH$_2$Cl$_2$–Et$_2$O mixtures afforded a yellow-brown crystalline material (yield 60%). The salt [PPh$_3$(CH$_2$Ph)][InCl$_2${Mo(CO)$_3$(η-C$_5$H$_5$)}$_2$] **16** was prepared in a similar manner except the product could only be obtained as an oily residue.

[NMe$_4$][InCl$_2${Mo(CO)$_3$(η-C$_5$H$_5$)}$_2$] **17**. A solution of Na[InCl$_2${Mo(CO)$_3$(η-C$_5$H$_5$)}$_2$] in thf (20 cm^3) was prepared as described previously[2] from InCl$_3$ (0.040 g, 0.181 mmol) and [Mo$_2$(CO)$_6$(η-C$_5$H$_5$)$_2$] (0.088 g, 0.181 mmol). To this was added a solution of [NMe$_4$]Cl (0.020 g, 0.181 mmol) in deoxygenated distilled water (5 cm^3), and the reaction solution was stirred for 18 h. During this time a colour change from yellow to dark yellow-brown was observed. The solvents were removed by vacuum and the resulting solid extracted in thf (10 cm^3) and filtered through Celite. The solvent volume was reduced to about 5 cm^3, over which hexane (30 cm^3) was layered. Solvent diffusion over a period of several days at −30 °C afforded yellow crystals which were isolated from the mother-liquor, washed with hexane and dried by vacuum (yield 49% based on InCl$_3$). Crystals of complex **17** produced in this way were suitable for X-ray diffraction.

[NEt$_4$][InI$_2${Mo(CO)$_3$(η-C$_5$H$_5$)}$_2$] **18**. The salt [NEt$_4$]I (0.061 g, 0.237 mmol) was added to a solution of [InI{Mo(CO)$_3$(η-C$_5$H$_5$)}$_2$] (0.173 g, 0.237 mmol) in thf (5 cm^3) at room temperature, and the resulting reaction mixture was stirred for 24 h. After this time a yellow solution was obtained together with a considerable amount of pale coloured solid. The thf was removed by vacuum and the yellow residue extracted in CH$_2$Cl$_2$ (10 cm^3) and filtered through Celite. The solvent volume was reduced by vacuum to 3 cm^3 over which hexane (20 cm^3) was layered. Solvent diffusion over a period of a few days at −30 °C afforded orange crystals, and a fluffy off-white solid which was washed out with hexane. The crystals were dried by vacuum (yield 55%).

[N(PPh$_3$)$_2$][InCl$_2${Cr(CO)$_3$(η-C$_5$H$_5$)}$_2$] **19**. The salt [N(PPh$_3$)$_2$]Cl (0.052 g, 0.090 mmol) was added to a stirred solution of [InCl{Cr(CO)$_3$(η-C$_5$H$_5$)}$_2$] **5** in thf (10 cm^3). The solution was stirred for 12 h during which time a colour change from yellow to green was observed. Removal of the thf by vacuum afforded a green oil which was redissolved in CH_2Cl_2 (2 cm^3). Yellow-green crystals were obtained as thin plates by solvent diffusion from either CH_2Cl_2–hexane or CH_2Cl_2–Et_2O mixtures at −30 °C over a period of 1–2 d (yield 74%).

$[PPh_3(CH_2Ph)][InCl_2\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]$ **20**. The complex $[InCl\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]$ **5** (0.050 g, 0.090 mmol) and $[PPh_3(CH_2Ph)]Cl$ (0.035 g, 0.090 mmol) were stirred in CH_2Cl_2 (4 cm^3) for 15 min. After this time the $[InCl\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]$ had completely dissolved and a yellow solution was obtained over which Et_2O (10 cm^3) and hexane (20 cm^3) were layered. Solvent diffusion over a period of 4 d at −30 °C afforded a lime-green oil which was isolated from the mother-liquor and stirred first in Et_2O (10 cm^3) and then hexane (20 cm^3) until a yellow powder was obtained. The Et_2O and hexane washings were discarded and the solid dried by vacuum. All attempts to recrystallise the compound were unsuccessful.

$[NMe_4][InCl_2\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]$ **21**. The salt $[NMe_4]Cl$ (0.012 g, 0.112 mmol) was stirred in CH_2Cl_2 (2 cm^3) and methanol was added dropwise until all the solid had dissolved. The solution was added to solid $[InCl\{Cr(CO)_3(\eta\text{-}C_5H_5)\}_2]$ **5**, affording a yellow-green solution over which Et_2O was layered. Solvent diffusion over a period of 4 d at −30 °C afforded small yellow crystals which were isolated from the mother-liquor, washed with hexane (3 × 5 cm^3) and dried under vacuum.

$Na/K[InCl_3\{Cr(CO)_3(\eta\text{-}C_5H_5)\}]$ **24**. A thf solution (20 cm^3) of $Na/K[Cr(CO)_3(\eta\text{-}C_5H_5)]$, derived from NaK (1:1) (0.3 cm^3) reduction of $[Cr_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (0.185 g, 0.460 mmol), was added to a stirred solution of $InCl_3$ (0.200 g, 0.902 mmol) in thf (10 cm^3) at 0 °C (ice-bath). On removal of the ice-bath the yellow reaction solution turned pale yellow-green, which darkened during stirring at room temperature for 1 h. No precipitate was observed during this time. The solvent volume was reduced to 5 cm^3, and the resulting lime-green solution set up to crystallise by solvent diffusion using hexane (25 cm^3) at −30 °C. After a period of a few days a pale yellow solid, a purple oil and a pale yellow mother-liquor were obtained. All solvents were removed by vacuum and the residue dissolved in thf (5 cm^3) to give a blue solution. Extraction in CH_2Cl_2, however, afforded a pale yellow solution from which, after filtration through Celite and solvent diffusion of hexane at −30 °C, small pale yellow crystals of $Na/K[InCl_3\{Cr(CO)_3(\eta\text{-}C_5H_5)\}]$ **24**, were formed after 4 d. A small amount of purple powder was washed away from the crystals in hexane. The crystals readily lost solvent on drying by vacuum (yield 10%).

$[Na(thf)][InI_3\{Mo(CO)_3(\eta\text{-}C_5H_5)\}]$ **25**. A stirred solution of InI_3 (0.084 g, 0.170 mmol) in thf (10 cm^3) was cooled to 0 °C and maintained at this temperature. To this was added a solution of $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$, derived from Na/Hg reduction of $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ (0.042 g, 0.085 mmol), also in thf (20 cm^3). The turbid yellow reaction solution was allowed to warm to room temperature, with continuous stirring for 2 h. The product was then worked up in one of two ways.

(1) The thf was removed by vacuum and the yellow residue extracted in CH_2Cl_2 (20 cm^3) and filtered through Celite. The yellow filtrate was reduced in volume to about 5 cm^3 over which hexane (30 cm^3) was layered. Solvent diffusion over 4 d at −30 °C afforded a yellow crystalline solid which was isolated from the mother-liquor, washed with hexane (10 cm^3) and dried by vacuum.

(2) Filtration of the reaction solution through Celite afforded a pale yellow filtrate which was reduced in volume to 3 cm^3. Crystallisation was effected by solvent diffusion of hexane (25 cm^3) over a period of several days at −30 °C. Initially the product started to form as an oil, but on continued storage at −30 °C yellow needles formed which were isolated from the mother-liquor and washed with hexane (2 × 10 cm^3). The crystals did not appear to lose solvent readily on drying by vacuum (typical isolated yield 53%).

$[InCl_2\{Mo(CO)_3(\eta\text{-}C_5H_4Me)\}]$ **26**. Indium monochloride (0.046 g, 0.306 mmol) and $[MoCl(CO)_3(\eta\text{-}C_5H_4Me)]$ (0.086 g, 0.306 mmol) were stirred in toluene (10 cm^3) at 75 °C (water-bath) for 2.5 h, affording a dark yellow-brown solution and a small amount of solid. The toluene was removed by vacuum and the yellow residue extracted in CH_2Cl_2 and filtered through Celite. Reduction of the solvent volume to 3 cm^3 followed by solvent diffusion using hexane (20 cm^3) at −30 °C afforded small yellow crystals of $[InCl_2\{Mo(CO)_3(\eta\text{-}C_5H_4Me)\}]$ **26**, in low yield.

$[InCl_2\{Mo(CO)(dppe)(\eta\text{-}C_5H_5)\}]$ **27**. Indium monochloride (0.031, 0.204 mmol) and $[MoCl(CO)(dppe)(\eta\text{-}C_5H_5)]$ (0.127 g, 0.204 mmol) were stirred in refluxing toluene (15 cm^3) for 5 h, during which time the solution changed colour from brick red to yellow, and the formation of a small amount of solid was observed. The toluene was removed by vacuum and the orange residue washed with toluene (2 × 10 cm^3) {orange washings, $[MoCl(CO)(dppe)(\eta\text{-}C_5H_5)]$ by infrared spectroscopy}. The resulting yellow powder was extracted in thf and filtered through Celite. Reduction of the solvent volume, followed by solvent diffusion using hexane, afforded yellow needles of $[InCl_2\{Mo(CO)(dppe)(\eta\text{-}C_5H_5)\}]$ **27**, after a period of a few days at −30 °C. The crystals lost solvent on removal from the mother-liquor and drying by vacuum.

$[In\{Mo(CO)_2(CNBu^t)(\eta\text{-}C_5H_5)\}_3]$ **28**. A stirred solution of $Na[Mo(CO)_2(CNBu^t)(\eta\text{-}C_5H_5)]$, derived from Na/Hg reduction of $[Mo_2(CO)_4(CNBu^t)_2(\eta\text{-}C_5H_5)_2]$ (0.284 g, 0.473 mmol), in thf (20 cm^3) was cooled to −78 °C and maintained at this temperature. To this was added a solution of $InCl_3$ (0.070 g, 0.316 mmol) in thf (10 cm^3) over a period of a few minutes with continuous stirring. During the addition a colour change from dark yellow-brown to dark yellow-orange was observed together with a formation of a fine, light-coloured precipitate. The reaction solution was allowed to warm slowly to room temperature and was stirred for 3 h. On removal of the thf by vacuum, a golden-brown solid was obtained which was extracted in CH_2Cl_2 and filtered through Celite. Reduction of the solvent volume to 5 cm^3 followed by solvent diffusion of hexane (30 cm^3) at −26 °C over a period of a few days afforded a dark yellow powder. Successive recrystallisations from CH_2Cl_2–hexane mixtures at −26 °C afforded a flaky golden-brown solid.

$[In\{Mo(CO)_2[P(C_6H_4Me\text{-}p)_3](\eta\text{-}C_5H_5)\}_3]$ **29**. This complex was prepared in a similar manner to **28** using $[Mo_2(CO)_4\{P(C_6H_4Me\text{-}p)_3\}_2(\eta\text{-}C_5H_5)_2]$, derived from $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ and $2P(C_6H_4Me\text{-}p)_3$. It was obtained as a yellow-brown powder from CH_2Cl_2–hexane mixtures (yield 79%).

Reaction between $[In\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$ *and* 0.5 $InCl_3$. A solution of $InCl_3$ (0.026 g, 0.118 mmol) in thf (5 cm^3) was added to a stirred solution of $[In\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_3]$ (0.201 g, 0.236 mmol) in thf (10 cm^3) at room temperature. The addition was accompanied by a decrease in the intensity of the yellow colour of the solution. Stirring was continued for 1.5 h after which time the thf was removed by vacuum. The oily residue was not very soluble in CH_2Cl_2, so recrystallisation was effected by solvent diffusion from thf–hexane mixtures at −30 °C. Compound **7** as a mixture of yellow plates and dark yellow blocks was isolated after several days.

Reaction between $InCl_3$ *and* $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$. Indium trichloride (0.066 g, 0.298 mmol) and $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ {prepared by refluxing $[Mo_2(CO)_6(\eta\text{-}C_5H_5)_2]$ in toluene} (0.129 g, 0.298 mmol) were stirred in refluxing toluene (20 cm^3) for 6 h, during which time a colour change from red-brown to yellow-brown was observed. The toluene was removed by vacuum, and the residue separated into three products by column chromatography (Florisil). The complex $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ was eluted as the major product in hexane, with small quantities of two yellow materials being eluted in Et_2O and thf respectively, the spectrum of one of which is described in the text.

Reaction between InCl *and* $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$. Indium monochloride (0.063 g, 0.419 mmol) and $[Mo_2(CO)_4(\eta\text{-}$

$C_5H_5)_2]$ (0.145 g, 0.335 mmol) were stirred in refluxing toluene. (An excess of InCl was used since some of it disproportionates to give indium metal and $InCl_3$.) After 6 h a yellow-brown solution was obtained. The toluene was removed by vacuum, and the residue redissolved in thf (10 cm^3), adsorbed onto Florisil and purified by column chromatography. The complex $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2]$ was eluted as the major product in hexane–Et_2O (1:1). A second, minor product was eluted in thf which is described in the text.

X-Ray Crystallographic Studies.—Crystal data for compound **4a**. Triclinic, $a = 10.815(3)$, $b = 12.589(3)$, $c = 13.799(4)$ Å, $\alpha = 109.21(1)$, $\beta = 98.40(1)$, $\gamma = 113.38(1)°$, $U = 1543.15$ Å^3.

Data collection. Insufficient data were collected for structure solution due to rapid crystal decay after 400 reflections (10% of total). Unit-cell data indicate that **4a** is isomorphous with **1a**.[2]

Crystal data for compound **7**. $C_{20}H_{18}ClInMo_2O_7$, $M_r = 712.51$, monoclinic, space group $P2_1/a$, $a = 16.217(6)$, $b = 9.048(3)$, $c = 17.246(5)$ Å, $\beta = 111.11(3)°$, $U = 2360$ Å^3, $Z = 4$, $D_c = 2.00$ g cm^{-3}, $F(000) = 1376$, μ(Mo-Kα) = 21.27 cm^{-1}.

Data collection and reduction. CAD4F Automated diffractometer with graphite monochromator. Crystal size 0.5 × 0.3 × 0.4 mm, $T = 295$ K, $2\theta_{max} = 50°$. Index ranges h 0–19, k 0–10, l −20 to 20, θ–2θ scan mode. Of 4594 reflections measured, 4136 were unique and 3182 with $F > 3\sigma(F)$ were used for structure determination. Lorentz polarisation and absorption/extinction[23] corrections applied (maximum and minimum corrections to transmission F 1.167 and 0.807 respectively).

Structure solution and refinement.[24] Atom positions determined by direct methods and difference syntheses and refined together with anisotropic thermal motion parameters for all non-H atoms to minimise $\Sigma w\Delta^2$; $\Delta = |F_o| - |F_c|$, $w^{-1} = \sigma^2(F_o)$. Hydrogen atoms constrained on ring-angle external bisectors with C–H 1.0 Å. For 280 refined parameters, $R = 0.034$, $R' = 0.039$. A final density difference synthesis showed no significant features. Scattering factors were taken from ref. 25 and all calculations were carried out on a MicroVAX 3600 using the Glasgow GX suite of programs.[26]

Although two distinctly different looking types of crystal were present in the batch, yellow blocks (a section of one of which was used for data collection) and yellow needles, unit-cell dimensions were the same for both.

Crystal data for compound **13**. $C_{21}H_{15}ClCr_2InNO_6$, $M_r = 631.62$, triclinic, space group $P\bar{1}$, $a = 8.100(1)$, $b = 8.820(1)$, $c = 16.162(2)$ Å, $\alpha = 94.87(1)$, $\beta = 93.45(1)$, $\gamma = 98.50(1)°$, $U = 1134.7$ Å^3 (from 2θ values of 32 reflections in 2θ range 20–25°), $Z = 2$, $D_c = 1.848$ g cm^{-3}, $F(000) = 620$, μ(Mo-Kα) = 20.67 cm^{-1}, $\lambda = 0.710\,73$ Å.

Data collection and reduction. Stoe-Siemens diffractometer with graphite monochromator. Crystal size 0.17 × 0.35 × 0.10 mm, $T = 295$ K, $2\theta_{max} = 45°$. Index ranges h −8 to 8, k −9 to 9, l 0–17, with equivalent reflections ($l < 0$), ω–θ scan mode, on-line profile fitting.[27] Of 3067 reflections measured, 2961 were unique and 2263 with $F > 4\sigma_c(F)$ were used for structure determination [$R_{int} = 0.056$, $\sigma_c(F)$ from counting statistics only]. Data corrected for Lorentz and polarisation effects, no significant crystal decay, and absorption (semiempirically); transmission factors 0.548–0.643. Extinction insignificant.

Structure solution and refinement.[28] Atom positions determined by Patterson and difference syntheses and refined together with anisotropic thermal motion parameters to minimise $\Sigma w\Delta^2$; $\Delta = |F_o| - |F_c|$, $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 13 - 43G + 84G^2 - 23H + 14H^2 + 14GH$ $(G = F_o/F_{max}$, $H = \sin\theta/\sin\theta_{max})$.[29] Hydrogen atoms constrained on ring-angle external bisectors with C–H 0.96 Å, $U(H) = 1.2U_{eq}(C)$. For 289 refined parameters, $R = 0.037$, $R' = 0.039$, goodness of fit = 1.083. A final difference synthesis contained maximum and minimum peaks at 1.11 and −0.51 e Å^{-3} close to the indium atom. Scattering factors taken from ref. 25.

Crystal data for compound **17**. $C_{20}H_{22}Cl_2InMo_2NO_6$, $M_r = 750.02$, monoclinic, space group $C2/c$, $a = 18.252(1)$, $b = 13.932(1)$, $c = 11.629(1)$ Å, $\beta = 115.11(1)°$, $U = 2677$ Å^3 (from 2θ values of 25 reflections with $2\theta > 20°$), $Z = 4$, $D_c = 1.868$ g cm^{-3}, $F(000) = 1456$, μ(Cu-Kα) = 169.60 cm^{-1}, $\lambda = 1.5418$ Å.

Data collection and reduction. Enraf-Nonius CAD-4F diffractometer with graphite monochromator, crystal size 0.22 × 0.24 × 0.27 mm, $T = 295$ K, $2\theta_{max} = 100°$, with indices $+h$, $+k$, $+l$, θ–2θ scan mode. Of 1718 reflections measured, 1326 were unique and 1163 with $F > 6\sigma(F)$ were used for structure determination ($R_{int} = 0.021$). Data corrected for Lorentz and polarisation effects. Empirical absorption corrections, transmission factors 0.42–0.99.

Structure solution and refinement.[28] Atom positions were determined by direct methods and difference syntheses and refined together with anisotropic thermal motion parameters for all non-H atoms to minimise $\Sigma w\Delta^2$ [$w^{-1} = \sigma^2(F) + 0.000\,625F^2$]. Two-fold disorder for the cation could not be resolved into two sites. Hydrogen atoms constrained in calculated positions. For 139 refined parameters, $R = 0.049$, $R' = 0.063$. The final difference synthesis contained maximum and minimum features at 1.24 and −1.14 e Å^{-3} close to the indium atom.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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